Self-Assembly of Oligosilane−Cyclodextrin Complexes Using Host-Stabilized π Interactions

Takanobu Sanji,*,† Masako Kato,‡ and Masato Tanaka*,†

Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan, and Department of Pure and Applied Chemistry, Tokyo University of Science, Noda 278-8510, Japan

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Introduction

Polysilanes have attracted considerable interest in the past few decades because of their interesting electronic and photophysical properties and because of their potential application as functional materials.[1] The unusual photophysical and electronic properties of polysilanes are attributable to the σ-conjugation occurring along the main chain, and hence, they are extremely sensitive to polymer conformation. Oligosilanes with well-defined structures are typical fundamental models for polysilanes, and several reports have addressed controlling the conformation of oligosilanes.[2,3] An example of controlling the conformation by inclusion into cyclodextrins (CyDs) has also reported.[4] Recently, we reported on the first example of the induction of a preferential helical-sense conformation in oligosilanes within the internal cavity of CyDs.[5,6]

CyDs[7] have a hydrophobic cavity that allows them to form stable inclusion complexes with a wide variety of guest molecules.[8] In particular, γ-CyD exhibits remarkable host−guest properties, including the encapsulation of two identical or different guest molecules inside the cavity to form a stable complex in which noncovalent interactions, such as $\pi-\pi$ stacking and charge transfer, are facilitated.[9]

We designed the oligosilane **1**, where the decasilane has a naphthyl group at a terminal position. Inclusion complexes occurring between **1** and CyDs can then assemble to form pseudorotaxane-type aggregates via host-stabilized π interactions,[10,11] which is the subject of this report. Supramolecular architectures have been of great interest in recent years because of their specific structure, properties, and functions.[12,13]

Results and Discussion

The oligosilane **1**, where the decasilane has a naphthyl group at a terminal position, was designed to assemble the pseudorotaxane-type aggregates via host-stabilized π interactions within the cavity of the γ-CyDs. The **1**/CyD (2/9) inclusion complex was prepared in a 77% yield by mixing **1** with a large excess of γ-CyD in water at room temperature for several days (Scheme 1). The molar ratio of **1**:γ-CyD, estimated using ^{1}H NMR spectroscopy (pyridine-d_5), was 2:9.[14] This suggests that the complex has a pseudorotaxane-type structure with face-to-face packing of the naphthyl groups in the γ-CyD cavities. On the basis of this molecular model, the molecular length of **1** was estimated to be ≈4 times the depth of the γ-CyD cavity (7 Å).

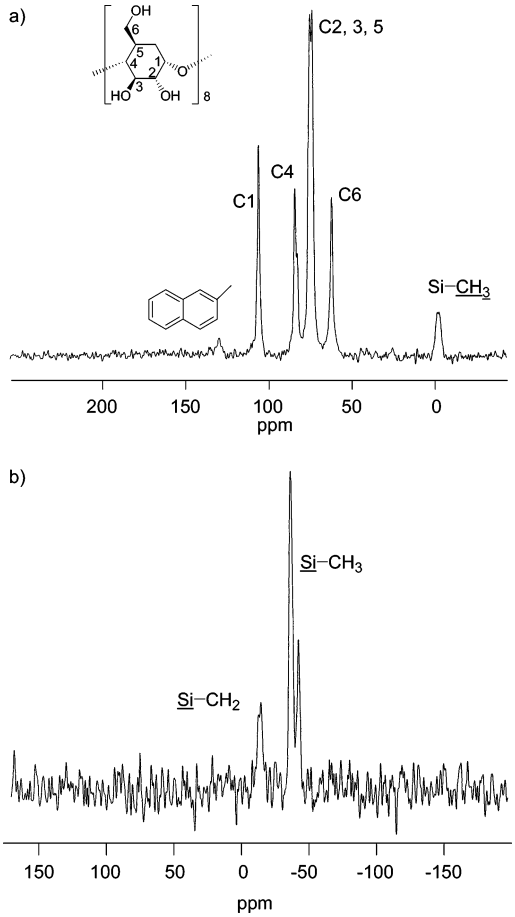
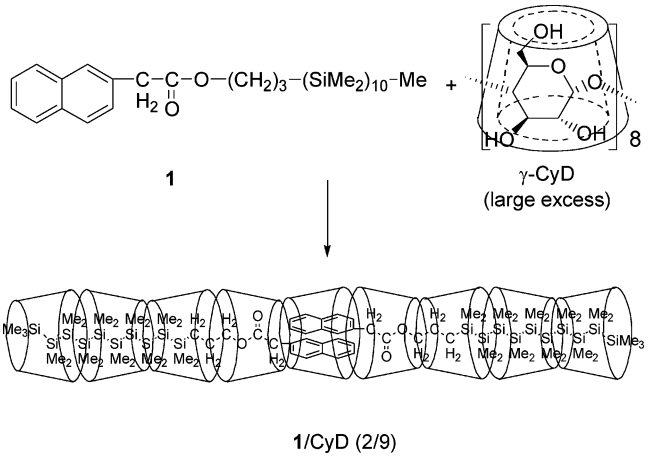


Figure 1. CP-MAS data: (a) ^{13}C and (b) ^{29}Si NMR spectra of **1**/CyD (2/9).

Scheme 1. Schematic Illustration of the Synthesis of the Inclusion Complex of 1/CyD (2/9)



Spectroscopic studies supported the structure of the **1**/CyD inclusion complex. In the CP-MAS ^{13}C NMR spectrum (Figure 1), the γ-CyD signals were more sharp as those of free γ-CyD, indicating that the γ-CyD adopted a symmetric conformation. In the CP-MAS ^{29}Si NMR spectrum, the peaks observed from −10 to −40

† Tokyo Institute of Technology.
‡ Tokyo University of Science.
* To whom correspondence should be addressed. E-mail: sanji@res.titech.ac.jp; m.tanaka@res.titech.ac.jp.

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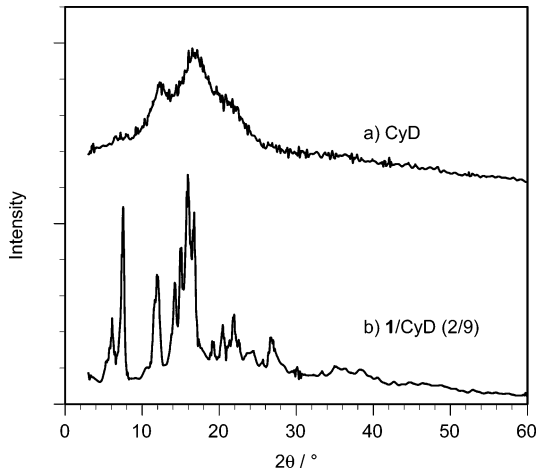

Figure 2. Powder X-ray diffraction patterns of (a) γ-CyD and (b) **1**/CyD (2/9).

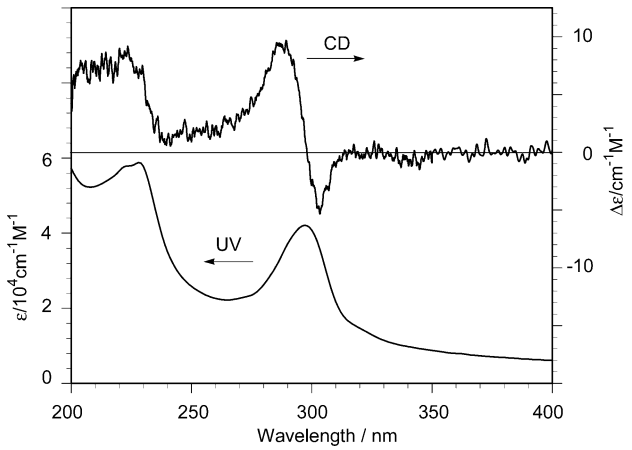

Figure 3. UV absorption and CD spectra of the **1**/CyD (2/9) complex in H_2O.

ppm were assigned to Me-*Si*. A powder X-ray diffraction (XRD) study showed that **1**/CyD was crystalline and that the XRD pattern was different from that of free γ-CyD (Figure 2). The XRD pattern of **1**/CyD showed a strong peak at $2\theta = 16°$ (Cu Kα), which is similar to that reported for a complex of γ-CyD exhibiting a channel-type structure.[15] These results indicate that an inclusion complex of **1** with γ-CyDs was formed.[16]

The **1**/γ-CyD complex was slightly soluble in water (up to concentrations of ca. 10^{-6} M), and hence, the spectroscopic properties of the complex in water could be successfully determined. In the UV spectrum of **1**/CyD (2/9) in H_2O (5×10^{-6} mol L^{-1}) at room temperature (Figure 3), two separate absorption bands corresponding to the individual absorption of the 2-naphthyl acetyl group ($\epsilon = 6.0 \times 10^4$ M^{-1} cm^{-1} at 224 nm) and the oligosilane ($\epsilon = 4.6 \times 10^4$ M^{-1} cm^{-1} at 297 nm) could be discerned. The absorption at 297 nm of the oligosilane due to the conjugated Si backbone $\sigma-\sigma^*$ transition overlapped with that of the naphthyl group. Since the molar extinction coefficient of permethyldecasilane ($\epsilon = 4.6 \times 10^4$ M^{-1} cm^{-1} at 284 nm) is much higher than that of naphthylacetic acid ($\epsilon = 500$ M^{-1} cm^{-1} at 273 nm) in hexane, the absorption of **1** occurring at around 290 nm was ascribed to the oligosilane. The absorption at 297 nm of the **1**/CyD complex is almost identical to the absorption of **1** in 3-methylpentane at 77 K, where the main chain assumes a predominantly *transoid* conformation with an Si tetrad dihedral angle of 160°−175° (15/7 helix),[17,18] while **1** in 3-methylpentane at room temperature showed an absorption maximum at 276 nm, where the main chain assumes a random-coil conformation. In the circular dichroism (CD) spectrum of a very dilute solution of the **1**/CyD (2/9) complex in H_2O (4.0×10^{-7} mol L^{-1}) using a longer path length cuvette (100 mm), the **1**/CyD (2/9) complex exhibited a positive CD band at about 290 nm ($\Delta\epsilon = 9.4$ M^{-1} cm^{-1} at 287 nm), which was associated with a weak negative CD band.[19] This indicates that the decasilane in the cavity of the γ-CyDs is induced to assume a preferential one-handed helical sense conformation leading to the observed optical activity. The dissymmetry ratio, g_{abs} ($= \Delta\epsilon/\epsilon$), is usually used to characterize helical structures such as right- and left-handed helix populations.[20] The **1**/CyD complex has a $g_{abs} = 2.0 \times 10^{-4}$. The value is the same order of magnitude ($(1-2) \times 10^{-4}$) observed for a range of polysilane with optically pure substituents which adopt preferential screw senses.[21] The origin of the weak band at around 305 nm exhibiting an opposite sign to the main peak in the CD spectra is unclear. When the decasilane moiety of the **1**/CyD complex adopts a preferential screw-sense helical motif, the decasilane should exhibit a single CD signal with either a positive or a negative sign only. Because of its poor solubility, the **1**/CyD (2/9) compound in water may produce certain aggregates, which may generate a bisignate CD signal. However, the UV and CD spectra of the complex measured in solution concentrations ranging from 10^{-7} to 10^{-6} M, or after filtration (pore size = 0.45 μm) to avoid any CD signal artifacts and any effect of self-absorption by **1** on the absorption spectrum, showed similar spectroscopic features. This finding may be correlated to more complicated features of the conformational effect on the spectra,[22] although a precise explanation requires further study.

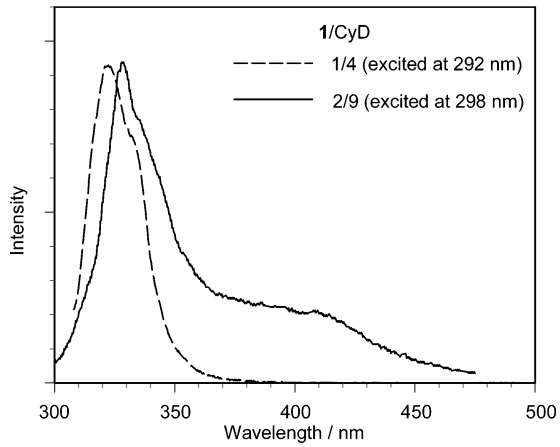

Figure 4. Fluorescence spectra of the **1**/CyD (2/9) and (1/4) complexes in H_2O.

The fluorescence of the **1**/CyD (2/9) complex supports the host-stabilized $\pi-\pi$ stacking of the naphthyl groups, as illustrated in Scheme 1. Thus, the **1**/CyD (2/9) complex excited at 292 nm exhibited an emission at 330 nm[17] and a broad emission at 420 nm[9] (Figure 4). The former emission was assigned to both the monomer fluorescence of the naphthyl group and the local emission from the oligosilane chain because the transition energies of the naphthyl group and the oligosilane chain are similar, while the latter emission was assigned to the dimer emission of the naphthyl groups.[23] The excitation spectra monitoring the emission at 450 nm

exhibited a new band at 350 nm, which was assigned to the ground-state dimer of the naphthyl groups in the γ-CyD.[9,24] The **1**/CyD (1/4) complex could be prepared as a reference compound by the reaction of **1** and γ-CyD in the mole ratio **1**:γ-CyD = 1:4.[25] The **1**/CyD (1/4) complex also showed a Cotton signal at about 295 nm.[26] However, only the monomer emission at 330 nm was observed. These results clearly support that the **1**/CyD (2/9) complex arranges to form a one-dimensional structure via $\pi-\pi$ stacking in the cavity of the CyDs.

Conclusions

We have demonstrated the self-assembly of oligosilane−cyclodextrin complexes induced by host-stabilized π interactions, in which the oligosilanes assume a preferential helical conformation. This is a simple way to control the conformation of oligosilanes and to align pseudo-polyrotaxane-type structures. For example, although it is difficult to form inclusion complexes with CyDs and high molecular weight polysilanes,[4,27] our new approach reported here is expected to provide pseudo-poly(oligosilanes).

Experimental Section

Materials and Measurements. The γ-cyclodextrin and 2-naphthylacetic acid used were obtained from the Tokyo Kasei Kogyo Co., Ltd. The 1-(3-hydroxypropyl)henicosamethyldecasilane used was prepared according to a previously reported procedure.[2a] The ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded using a Bruker DPX 300 FT-NMR spectrometer at 300, 75.4, and 59.6 MHz, respectively. The ^{1}H and ^{13}C chemical shifts were referenced to solvent residues (^{1}H, δ = 7.24 ppm, and ^{13}C, δ = 77.0 ppm for $CDCl_3$). The ^{29}Si chemical shift was referenced to an external Me_4Si (0 ppm) reference. The GLC data were recorded using a Shimadzu GC-8A chromatograph. The ^{13}C and ^{29}Si CP-MAS NMR spectra were measured at 67 and 53.5 MHz, respectively, using a JEOL Excalibus 270 spectrometer. The X-ray diffraction patterns were recorded using a Rigaku RAXIS-IIc X-ray diffractometer. The UV spectra were recorded using an HP Agilent 8453 spectrometer. The fluorescence spectra were recorded using an Hitachi F 4500 spectrometer. The CD spectra were obtained using a JASCO J-820 spectrometer.

Preparation of 1-(2′-Naphthylacetoxypropyl)henicosamethyldecasilane, 1. A mixture of 1-(3-hydroxypropyl)-henicosamethyldecasilane (1.0 g, 1.53 mmol), 2-naphthylacetic acid (0.29 g, 1.53 mmol), (dimethylamino)pyridine (0.1 g, 0.817 mmol), and dicyclohexylcarbodiimide (0.525 mg, 2.54 mmol) in toluene (10 mL) was stirred at room temperature for 18 h. After filtration of the white solid obtained, the mixture was washed successively with water and saturated NaCl solution and then evaporated after being dried over anhydrous $MgSO_4$. The residue was chromatographed over silica gel with toluene to give 1 (0.93 g, 1.11 mmol). **1**: yield = 73%; white solid; mp = 97−113 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.027 (s, 6H), 0.075 (s, 9H), 0.097 (s, 6H), 0.12 (s, 6H), 0.14 (s, 6H), 0.17−0.19 (m, 30H), 0.51−0.57 (m, 2H), 1.61 (tt, J = 6.8 and 6.9 Hz, 2H), 3.77 (s, 2H), 4.05 (t, J = 6.8 Hz, 2H), 7.39−7.47 (m, 3H), 7.72 (s, 1H), 7.79 (d, J = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ −5.19, −4.85, −3.86, −3.82, −3.58, −3.56, −2.89, −1.17, −0.82, 11.8, 24.2, 42.1, 68.0, 126.2, 126.3, 126.5, 127.8, 128.1, 128.4, 128.6, 132.1, 132.9, 133.8, 172.1. ^{29}Si NMR ($CDCl_3$, 59.6 MHz): δ −43.2, −43.0, −38.9, −37.8, −37.6, −37.5, −37.4, −37.4, −15.0, −12.9. Anal. Calcd (%) for $C_{36}H_{78}O_2Si_{10}$: C, 52.55; H, 9.50. Found (%): C, 52.71; H, 9.19.

Preparation of the Inclusion Compound (1/CyD (2/9)). A mixture of **1** (100 mg, 0.122 mmol) and γ-cyclodextrin (1.58 g, 1.22 mmol) in 15 mL of water was stirred at room temperature for 48 h. The white precipitate containing the product was collected by centrifugation and washed with water and then with THF. The residue was dried under vacuum to give the inclusion complex **1**/CyD as a white powder (618 mg, 77%). The molar ratio of **1**:γ-CyD estimated from ^{1}H NMR (pyridine-d_5) data was 2:9. **1**/CyD (2/9): white powder; mp = 216−254 °C (decomposition). ^{1}H NMR (pyridine-d_5, 300 MHz): δ 0.14 (s, 6H), 0.18 (s, 9H), 0.25 (s, 12H), 0.28−0.37 (m, 36H), 0.64−0.70 (m, 2H), 1.70−1.75 (m, 2H), 3.63 (t, J = 6.3 Hz, 2H), 3.97 (s, 2H), 4.09 (s, 8H × 4.5), 4.21−4.31 (m, 36H), 4.34−4.43 (m, 24H × 4.5), 4.63 (t, J = 9.1 Hz, 36H), 5.72 (d, J = 3.4 Hz, 36H), 6.42 (br, 36H), 7.47 (t, J = 3.8 Hz, 3H), 7.68 (s, 16H × 4.5), 7.84−7.89 (m, 4H). ^{13}C CPMAS NMR (67 MHz): δ −2.63, −1.77, 61.1, 72.6, 73.9, 83.1, 105, 128. ^{29}Si CPMAS NMR (53.5 MHz): δ −42.9, −37.0, −14.5, −12.8.

Preparation of the Inclusion Compound (1/CyD (1/4)). **1**/CyD (1/4) was prepared using the same method as described for **1**/CyD (2/9), using a different mole ratio **1**:γ-CyD = 1:4. 1/CyD (1/4): yield 74%; white powder; mp = 221−264 °C (decomposition). ^{1}H NMR (pyridine-d_5, 300 MHz): δ 0.138−0.236 (m, 18H), 0.266 (s, 6H), 0.276−0.297 (m, 9H), 0.310−0.372 (m, 30H), 0.853−0.910 (m, 2H), 1.80−1.90 (m, 2H), 3.91 (t, J = 6.6 Hz, 2H), 4.09 (s, 8H × 4), 4.25−4.34 (m, 32H), 4.38−4.43 (m, 24H × 4), 4.64 (t, J = 9.2 Hz, 32H), 5.73 (d, J = 3.6 Hz, 32H), 6.40 (br, 32H), 7.68 (s, 16H × 4). ^{13}C CPMAS NMR (67 MHz): δ −1.70, 12.9, 28.3, 61.1, 65.2, 73.5, 83.0, 105. ^{29}Si CPMAS NMR (53.5 MHz): δ -42.5, −37.1, −12.5.

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References and Notes

(1) For a review of polysilanes, see: Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359.

(2) (a) Mazières, S.; Raymond, M. K.; Raabe, P. A.; Michl, J. *J. Am. Chem. Soc.* **1997**, *119*, 6682. (b) Tamao, K.; Tsuji, H.; Terada, M.; Asahara, M.; Yamaguchi, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 3287. (c) El-Sayed, I.; Hatanaka, Y.; Onozawa, S.; Tanaka, M. *J. Am. Chem. Soc.* **2001**, *123*, 3597.

(3) (a) Fujiki, M. *J. Am. Chem. Soc.* **1994**, *116*, 11976. (b) Koe, J. R.; Fujiki, M.; Nakashima, H. *J. Am. Chem. Soc.* **1999**, *121*, 9734. (c) Obata, K.; Kira, M. *J. Am. Chem. Soc.* **1997**, *119*, 11345.

(4) (a) Okumura, H.; Kawaguchi, Y.; Harada, A. *Macromol. Rapid Commun.* **2002**, *23*, 781. (b) Okumura, H.; Kawaguchi, Y.; Harada, A. *Macromolecules* **2003**, *36*, 6422. (c) Sakamoto, K.; Naruoka, T.; Kira, M. *Chem. Lett.* **2003**, *32*, 380.

(5) Sanji, T.; Yoshiwara, A.; Sakurai, H.; Tanaka, M. *Chem. Commun.* **2003**, 1506.

(6) Recently, several reports have addressed optically active induction in poly(phenylacetylene) with a β-CyD as the side chain and the complex between a γ-CyD and poly(methacrylic acid) with a binaphthyl side chain. See: (a) Yang, S. Y.; Green, M. M.; Schultz, G.; Jha, S. K.; Müller, A. H. E. *J. Am. Chem. Soc.* **1997**, *119*, 12404. (b) Yashima, E.; Maeda, K.; Sato, O. *J. Am. Chem. Soc.* **2001**, *123*, 8159.

(7) For a recent review on cyclodextrins, see: *Chem. Rev.* **1998**, *98*, 1741 (special issue).

(8) Harada, A. *Acc. Chem. Res.* **2001**, *34*, 456.

(9) (a) Ueno, A.; Takahashi, K.; Osa, T. *J. Chem. Soc., Chem. Commun.* **1980**, *921.* (b) Ikeda, H.; Iidaka, Y.; Ueno, A. *Org. Lett.* **2003**, *5*, 1625.

(10) For a pioneering work on asymmetric encapsulation for the polymerization of pentadiene in perhydrotriphenylene cavities to make optically active polymers, see: (a) Farina, M.; Audisio, G.; Natta, G. *J. Am. Chem. Soc.* **1967**, *89*, 5071. (b) Farina, M.; Pedretti, U.; Gramegna, M. T.; Audisio, G. *Macromolecules* **1970**, *3*, 475.

(11) The synthesis of poly(polyrotaxane) has been reported recently: (a) Okada, M.; Harada, A. *Macromolecules* **2003**, *36*, 9701. (b) Okada, M.; Harada, A. *Org. Lett.* **2004**, *6*, 361.

(12) (a) Moore, J. S. *Curr. Opin. Colloid Interface Sci.* **1999**, *4*, 108. (b) Brunsveld, L.; Folmer, B. J.; Meijer, E. W.; Sijbesma, R. P. *Chem. Rev.* **2001**, *101*, 4071.

(13) (a) Li, G.; McGown, L. B. *Science* **1994**, *264*, 249. (b) Yamaguchi, I.; Yamamoto, T. *Chem. Lett.* **2002**, 938.

(14) The inclusion complex may dissociate in pyridine-d_5.

(15) (a) Steiner, T.; Saenger, W. *Acta Crystallogr.* **1998**, *B54*, 450. (b) Harada, A.; Li, J.; Suzuki, S.; Kamachi, M. *Macromolecules* **1993**, *26*, 5267.

(16) However, we have no mass spectrometric data of the proposed structure with MALDI-TOF MS or ESI MS probably due to their quite delicate structures. Further work to obtain the mass data is required.

(17) Obata, K.; Kira, M. *Organometallics* **1999**, *18*, 2216.

(18) Michl, J.; West, R. *Acc. Chem. Res.* **2000**, *3*, 821.

(19) The naphthylacetic acid in γ-CyD shows a positive Cotton signal at 220 nm ($\Delta\epsilon \approx 10$ M^{-1} cm^{-1}) but does not show a Cotton signal at around 300 nm under the same conditions ($\Delta\epsilon < 0.5$ M^{-1} cm^{-1}).

(20) Fujiki, M. *Macromol. Rapid Commun.* **2001**, *22*, 539.

(21) (a) Fujiki, M. *J. Am. Chem. Soc.* **1994**, *116*, 6017. (b) Toyoda, S.; Fujiki, M. *Macromolecules* **2001**, *34*, 640.

(22) (a) Albinsson, B.; Teramae, H.; Downing, J. W.; Michl, J. *Chem.—Eur. J.* **1996**, *2*, 529. (b) Imhof, R.; Teramae, H.; Michl, J. *Chem. Phys. Lett.* **1997**, *270*, 500.

(23) The ratio of the excimer emissions is not very high when the two naphthyl groups of the **1**/CyD (2/9) complex adopt face-to-face packing in the CyD cavity. It is probable that all the axial molecules of **1** may not be aligned in an effective head-to-head fashion, although a detailed explanation of the structure of the **1**/CyD complex requires further study.

(24) (a) Herata, K.; Uedaira, H. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 375. (b) Yorozu, T.; Hoshino, M.; Imamura, M.; Shizuka, H. *J. Phys. Chem.* **1982**, *86*, 4422.

(25) Although no critical ratio of **1**:CyD was found, **1**/CyD (2/9) was formed in the reaction of γ-CyD with **1** in a mole ratio >10.

(26) In the CD spectra, the (1/4) complex did not show a CD signal at 220 nm, as was observed for the (2/9) complex, indicating that the naphthyl group of the (1/4) complex is probably not encapsulated by CyDs.

(27) A mixture of polysilane ($M_w = 2000$) and γ-CyD gave the inclusion complex in a 4% yield: Sanji, T.; Kato, M.; Tanaka, M., unpublished results.

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